CO$_2$ mass transfer model for carbonic anhydrase-enhanced aqueous MDEA solutions

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ABSTRACT

In this study a CO$_2$ mass transfer model was developed for carbonic anhydrase-enhanced MDEA solutions based on a mechanistic kinetic enzyme model. Four different enzyme models were compared in their ability to predict the liquid side mass transfer coefficient at temperatures in the range of 298–328 K, solvent concentrations in the range 15–50 wt%, CO$_2$ partial pressures up to 50 kPa, solvent loading between 0 and 0.5 mol CO$_2$ per mole MDEA and enzyme concentrations up to 8.5 g/L. The reversible Michaelis Menten model (MR) and the simplified model with product inhibition by the bicarbonate ion (SP) were able to predict the mass transfer with an absolute average relative deviation of less than 15%. The MR model could account for every influence (solvent concentration, temperature, solvent loading, CO$_2$ partial pressure) of the different process conditions on the mass transfer, whereas the SP model is limited to applications with low CO$_2$ partial pressure such as CCS from coal burning power plants. Two other models that were also investigated are not suitable for implementation into an absorber column simulation, as they cannot describe the influence of changing solvent loading on the mass transfer.

1. Introduction

Reactive absorption technology can be applied for carbon capture in post combustion at large point sources such as fossil fuel-burning power plants. In the near future it can help to achieve the ambitious goals in greenhouse gas reduction while also ensuring a safe and stable energy supply. This technology is already applied in several industrial processes where mixed gas streams are cleansed of CO$_2$, such as in natural gas treatment, biogas purification, synthesis gas production and ammonia production. However, there are still challenges for application in post combustion, because of the large gas volumes to be treated, and the low concentration of CO$_2$ in the exhaust gases.

For processes with very low CO$_2$ driving forces reactive (also called chemical) absorption technology is suitable as the mass transfer rates are enhanced by a chemical reaction. The reaction is crucial. It depletes the CO$_2$ near the interface which results in higher diffusion and therefore enhances the mass transfer. The absorption in CCS applications are carried out in kinetically controlled regimes, thus the reaction rates are primarily influencing the mass transfer rates.

In a general process outline a chemical solvent is introduced into the absorber column at the top. It is called the lean solvent, since the CO$_2$

content, comprising of physical bound CO$_2$ and various reaction products is low. The flue gas coming from the power plant exhaust is blown by a fan from the bottom of the absorber through the column with a counter-currently descending liquid flow in contact. CO$_2$ from the gas is dissolved in the liquid and reacts with the solvent forming carbamates, and/or bicarbonates. The "rich" solvent, with high amount of chemically bound CO$_2$ leaves the absorber bottom. It is pumped into the desorber, where the chemical and thermodynamic equilibrium are shifted by an increase in temperature and CO$_2$ is released from the solvent.

In order to optimize the process, capital and operating costs should be minimized. For lower capital costs the equipment size should be reduced. The size of the absorber, which has the highest contribution to the overall capital costs in a conventional system, can be reduced if the mass transfer can be increased. This can be achieved by higher reaction rates of the solvent with CO$_2$. For optimizing the operating costs, the heat requirement in the desorber should be targeted, as it makes up to 90% of the total operating costs, excluding the compression stage [1]. It remains a big challenge to optimize capital costs and operating costs together, as there is a relation between reaction speed and heat of reaction [1]. This implies that fast reacting solvents which result in

smaller mass transfer equipment and lower capital costs need more energy in the reboiler to reverse the reactions. On the other hand, solvents with low heat of reaction are very slow absorbing and thus lead to uneconomical equipment sizes.

The use of catalysts can speed up the reactions rates of slow solvents while maintaining the low heat of reaction. One catalyst which increases the reversible reaction rate between CO_2 and water is the enzyme carbonic anhydrase (E.C.4.2.1.1.) (CA) [2]. The aim of this study is to derive a mechanistic kinetic model for the catalyzed reactions by CA in the tertiary amine MDEA from CO_2 mass transfer experiments. The model should be capable, once implemented in a column model to predict the mass transfer accurately across a wide range of process conditions, such as varying temperature, solvent concentration, solvent loading and enzyme concentration for both absorption and desorption.

2. Enzymes

Enzymes are biological catalysts that reduce the activation energy of (bio)chemical reactions. The main advantages for enzyme based catalysis compared to conventional catalysts are the high regio- and stereoselectivity, the possibility to perform the reaction in mild conditions, which therefore needs less energy (e.g. lower process temperature), and low by-product generation.

However, enzymes are also unstable at certain process conditions. Their stability is dependent on pH, temperature and salt or organic compound concentration.

2.1. CA mechanism

The CA enzyme was discovered when the high mass transfer rates of CO_2 in blood were investigated by Meldrum and Roughton [4]. The interconversion of CO_2 and bicarbonate catalyzed by carbonic anhydrase could explain why CO_2 mass transfer rates higher than physical absorption could be obtained. The overall reaction of CA enzyme observed was:

$$CO_2 + H_2O \overset{CA}{\longleftrightarrow} HCO_3^- + H^+ \tag{1}$$

The active site of carbonic anhydrase is a Zn^{2+} ion with an attached

hydroxyl group. The reaction mechanism of α-CAs is well studied; a scheme is shown in Fig. 1. The figure is adapted from Pierre [5] to show the mechanism from a different angle, as it includes the proton channel into the overall reaction mechanism. Even though the β- and γ-family have different protein sequence, the main mechanism of CO_2 hydration shows similarities concerning the rate limiting steps [6,7]. All CA types involve a CO_2 hydration of a zinc bound hydroxide ion as well as a proton removal from water bound to zinc and proton transfer to a side amino acid chain [8].

The pictogram in Fig. 1 show a CA enzyme is in its active state with a hydroxide ion bound to zinc and a CO_2 molecule nearby (A), the amino acid side chain, here referred to as proton channel (PC) is releasing a proton to a buffer molecule in the solution, in the intermolecular proton transfer. The zinc bound hydroxyl then reacts with the nearby carbon dioxide molecule via a nucleophilic attack onto the C-atom (B) resulting in a zinc-bound bicarbonate. The bicarbonate is swapped by a water molecule releasing bicarbonate to solution (C), leaving the enzyme in an inactive state with water bound to the zinc (D). To regain its catalytic activity one proton has to be removed from the zinc-bound water molecule. The proton is transferred via PC; this step is called the intramolecular proton transfer. This transfer occurs over intervening hydrogen bonded water molecules as the two functional groups are not close to each other. The transfer involves between 2 and 3 water molecules for α-CA [7,9], although this value might vary for different enzymes.

As the buffer concentration must be lower than 10 mM [10] to make the intermolecular proton transfer rate limiting, in carbon capture applications with solvent concentration in the order of 1 M the rate limiting step is considered to be the transfer of the proton to the side chain PC. The overall reaction can then be described as:

$$CO_2 + H_2O + B \overset{CA}{\longleftrightarrow} HCO_3^- + BH^+ \tag{2}$$

B represents any kind of proton acceptor such as hydroxyl ions or a base. The enzyme catalyzes the reversible reactions towards the chemical equilibrium. If the concentration of bicarbonate is lower than the chemical equilibrium, CO_2 is consumed. If it is higher, CO_2 will be produced from bicarbonate and the reaction follows a counterclockwise path in Fig. 1.

Fig. 1. Reaction mechanism of α-carbonic anhydrase, adapted from Pierre [5].